

Synthesis of Imidazolidine 2,4 – Dione Derivatives

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Abstract:

Synthesis routes to diphenyl hydantion derivatives in the presence of the benzils ; 4,4 – dimethyl benzyl , 4- amino benzil , 4,4- dichloro benzil , 4,4- dibromo benzil , urea , methyl urea and ethyl urea – give condensation derivatives of benzil and alkyl urea by benzylic rearrangement .

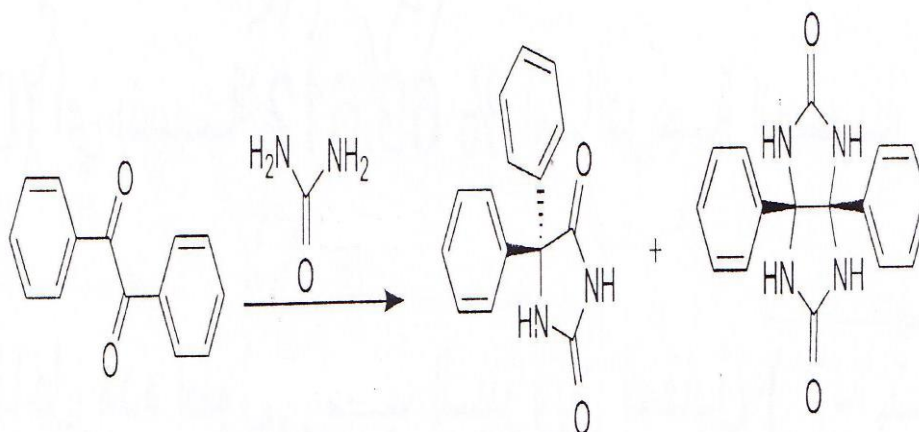
Introduction:

The imidazolidine 2,4 – dione , or hydantion nucleuc is acommon 5- membrane is present in a wide range of biologically active compounds including antiarr by times anticonvulsant and autitumor agents (1 – 6) .

The most straight forward condition for the synthesis of phenytion is the base – catalysed condensation using benzyl and urea



Scheme (1)



Known as the Biltz synthesis of phenytion . Dunnavanl and James showed that the reaction proceeds via a benzylic rearrangement and several 1,5- diphenyl hydoutions

Experimental

Melting points were determined using an electrothermal digital melting point apparatus . I.R spectra were measured in pye Unicom 9712 spectra photometer in KBr . H n.m.r spectra were measured with Hitacha R- 24 B (300 MHz) in cDCl₃ with TMS as internal standard .

General Procedures

Synthesis of Imidazolidine 2,4 – Dione Derivatives (7 , 8)

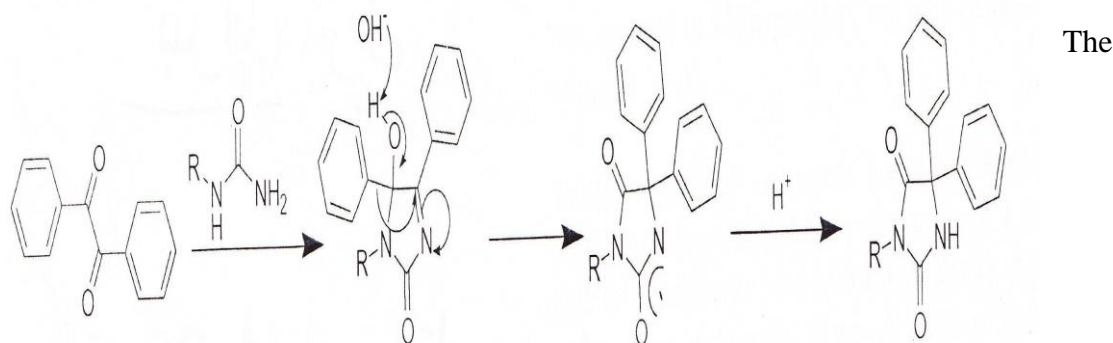
To a solution of 20.2 gm of benzil (96.2 m mole) and 12.69 gm of urea (167 m mole) in 40 ml of DMSO 25 ml of 1.2 M aqueous KOH were added under stirring . The resulting mixture was refluxed for 2h and poured into cold water .

The precipitate was filtrated and the filtrate was acidified with glacial acetic acid . The resulting precipitate was collected dried and recrystallized from ethanol .

RESULTS AND DISCUSSION

The Biltz synthesis(9,10) is a common way to synthesis phenytion (x = o) starting from symmetrical and symmetrical benzil and urea formation (a) and (b) scheme 1

The mechanism (scheme 2) is similar to the mechanism - the classical Biltz synthesis of phenytion .



Scheme (2)
Mechanism of condensation of benzile and urea

result show thtransportation of predicated neighboring groups depend on their nucleophilicity(11,14). For the substitute group in the para position and meta position , while the ortho position is steric factor . And there are two interpretations for this reaction either phenium ion or ionization state , but most scientists supports the first opinion .

The subsequent conversion in to phenytion resulting in the virtual absence of glycolureide side (b) . Finally , the imiduzolidine were obtained from the 4,4⁻ - dibromo benzil 5,5 – Bis – (4- bromo – phynyl) – imiduzolidine,2,4 – dione 5,5⁻ - Bis-(4-bromo-phenyl)- 3 methyl - imiduzolidine 2,4–dione (2b)

5,5 - Bis (4-bromo - phenyl)-3- methyl - imiduzolidine 2,4-dione(3c). All the analysis fit the product table (1,2 and 3) and imiduzolidine were obtained from the 4-4- - dichloro benzil
5,5 - Bis - (4-chloro-phenyl) - imiduzolidine 2,4- dione (2a)
5,5 - Bis - (4-chloro-phenyl) -3- methyl- imiduzolidine 2,4- dione (2b) and
5,5 - Bis - (4-chloro-phenyl) -3- methyl- imiduzolidine 2,4- dione (2c) . All the analysis fit the product table (1,2 and 3) it is worth mentioning that the imiduzolidine were obtained from 4,4- dimethyl benzil and 4- amino benzil reaction with urea and methyl urea give (3a,3b) , and (4a,b) . All the analysis fit the product table (1,2 and 3)

Table (1)
Analytical data of the imidazolidine derivatives

Compd .	Formuta M.W	Calculated % found		
		C	H	N
1- 5,5 -Bis(4-bromophenyl) -imidazolidene-2,4- dione(1a)	C ₁₅ H ₁₀ Br ₂ N ₂ O ₂	43.69	2.42	6.79
2- 5,5 -Bis(4-bromo-phenyl) -3-methyl-imidazolidine-2,4- dione(1b)	C ₁₆ H ₁₂ Br ₂ N ₂ O ₂	45.32	2.85	6.61
3- 5,5 -Bis(4-bromo-phenyl) -3-ethyl-imidazolidine-2,4- dione(1c)	C ₁₇ H ₁₄ Br ₂ N ₂ O ₂	46.61	3.22	6.39
4- 5,5 -Bis(4-chloro-phenyl) -imidazolidene-2,4- dione(2a)	C ₁₅ H ₁₀ Cl ₂ N ₂ O ₂	56.07	3.11	8.72
5- 5,5 -Bis(4-chloro-phenyl) -3-methyl-imidazolidine-2,4- dione(2b)	C ₁₆ H ₁₂ Cl ₂ N ₂ O ₂	57.31	3.58	8.35
6- 5,5 -Bis(4-chloro-phenyl) -3-ethyl-imidazolidine-2,4- dione(2c)	C ₁₇ H ₁₄ Cl ₂ N ₂ O ₂	58.47	4.04	8.02
7- 5,5 -Bis(4-methyl-phenyl) -imidazolidine-2,4- dione(3a)	C ₁₇ H ₁₄ Cl ₂ N ₂ O ₂	58.27	4.11	7.96
8-5,5 -Bis(4-methyl-phenyl) -3-methyl-imidazolidine-2,4- dione(3b)	C ₁₈ H ₁₆ N ₂ O ₂		5.71	10.00
9- 5-Bis(4-amino-phenyl) -5-phnyl-imidazolidine-2,4- dione(4a)	C ₁₇ H ₁₆ N ₂ O ₂	72.75	5.66	9.97
10- 5-Bis(4-amino-phenyl) -5-phnyl-3-methyl-imidazolidine-2,4- dione(4b)	C ₁₈ H ₁₄ N ₂ O ₂	74.98	4.82	9.65
	C ₁₅ H ₁₃ N ₃ O ₂	67.41	4.86	9.65
		66.98	4.76	9.55
	C ₁₆ H ₁₆ Br ₂ N ₃ O ₂		5.67	14.89
		68.18	5.57	14.29

Table (2)
I R Spectral data of the imidazolidine derivatives

Comp	I R Cm ⁻¹
1a	3218(NH) , 1769(c=o) , 1710(c=o) , 1480(c=c)
1b	3211(NH) , 1772(c=o) , 1712(c=o) , 1480(c=c)
2a	3210(NH) , 1775(c=o) , 1710(c=o) , 1489(c=c)
2b	3210(NH) , 163(c=o) , 1710(c=o) , 1490(c=c)
2c	3215(NH) , 1766(c=o) , 1711(c=o) , 1496(c=c)
3a	3211(NH) , 1765(c=o) , 1712(c=o) , 1490(c=c)
4a	3377(NH) , 1692(c=o) , 1670(c=o) , 1488(c=c)

Table (3)
H-NMR Spectra of the imidazolidine derivatives in CDCl₃

Comp	H-NMR (Sppm ; Jin Hz)
1b	2.93(m-3H) , 7.30(d.4H) , 7.61(d.4H) , 9.69(s.1H)
1c	1.07 - 1.12(m,3H) , 3.44 - 3.51(m.2H) , 7.28(d.4H) , 7.63 (d4H)9.70(s.1H)
2b	7.36(d,4H) , 7.49(d,4H) , 9.40(s,1H)

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تحضير مشتقات الايمدازولين 2 ، 4 ثنائي كيتون

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قسم الكيمياء

الخلاصة

الهدف من هذا البحث هو تحضير مشتقات الأيمدازول من تفاعل مركبات البنزويل المو 4، 4- ثنائي برومو بنزويل، 4، 4- ثنائي للوروبنزويل ، 4، 4- ثنائي مثيل بنزويل ، 4- امينو بنزويل مع مركبات اليوريا واثيل اليوريا اعطت مجموعة من المشتقات شخصل هذه المركبات بواسطة التقنيات التالية C.H.N واطياف الاشعة الحمراء وطياف الرنين النووي المغناطيسي .